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SiC-TiSi₂ materials codeposited by CVD

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Abstract

SiC - TiSi₂ composites were prepared by CVD under atmospheric pressure at 850°C using the TiCl₄ - SiH₂Cl₂ - C₄H₁₀ - H₂ gas system. Thermodynamical calculation trends, dealing with the influence of the initial gas phase composition on the amount of TiSi₂ were compared with the experiments. Codeposits were texture-free. Apparent crystallite size was ranging between 20 to 50nm. Intrinsic hardness deduced from the extrapolation at infinite load of measured values, fitted well with that given by a rule mixture: $H_{\infty} = V_{TiSi_2} \cdot H_{TiSi_2} + (1 - V_{TiSi_2}) \cdot H_{SiC}$. Using indentation technique, median-radial crack system was observed. Values of toughness were about 35 to 50 % greater than for a pure SiC-CVD depending on the amount of TiSi₂.

1.- Introduction

Chemical vapor deposition (CVD) is an efficient method for creating ceramic composite architectures with an extremely uniform dispersion of the reinforcement compound when codepositing the ceramic matrix.

Little work on the use of CVD for this purpose has been published [1-6]. In the chemical system Ti-Si-C, fine SiC particles uniformly dispersed in a TiC matrix have been codeposited at reduced pressure (0.4 atm) in the temperature range 1573-1873 K [7]. These composites had a fracture toughness value [8] higher than 10 MPa.m^{1/2}. More recently, SiC-based composites with TiC as dispersed ceramic have been elaborated [9] at 1623 K and 0.08 atm. The K_{IC} of these materials [10] which presented a columnar microstructure, was about 12 MPa.m^{1/2}. Other binary mixtures in the Ti-Si-C system were also deposited by CVD. Dispersed TiSi₂ in a SiC matrix has been obtained at 1673 K and atmospheric pressure [11]. The fracture toughness values were close to 5.5 MPa.m^{1/2} for the best coatings. The deposition of materials composed of alternating platelets of Ti₃SiC₂ and SiC was also mentioned [12].

The main objective of the present work was to prepare an homogeneous dispersion of TiSi_2 in a SiC matrix by CVD under atmospheric pressure at the temperature of 850°C .

2.- Experimental procedure

Deposits were prepared in a cold-wall reactor ($\varnothing = 6.2$ cm., $L = 20$ cm), on polycrystalline graphite substrates mechanically polished (thickness = 1.2 mm) (le Carbone-Lorraine 1116 PT). The substrates resistively heated had a shape specially designed in order to obtain a uniformly heated zone of 25×5 mm². The initial gaseous mixture was composed of TiCl_4 , C_4H_{10} , SiH_2Cl_2 and H_2 (flow rate 30 l/h or 40 l/h [13]). A set of thirteen samples (figure 1) of different compositions were prepared at atmospheric pressure by varying at 850°C the composition of the input gas species in the range: $0.0030 \leq X_{\text{TiCl}_4} \leq 0.0057$, $0.0171 \leq X_{\text{SiH}_2\text{Cl}_2} \leq 0.0377$, $0.0150 \leq X_{\text{C}_4\text{H}_{10}} \leq 0.0313$ and $0.94 \leq X_{\text{H}_2} \leq 0.96$ (in molar fractions). The deposition time was 0.5 h.

Coating thicknesses were ranging from 50 to 100 μm depending on the experimental conditions.

Figure 1: Variation of composition of the sixteen SiC - TiSi_2 codeposits.

3.- Experimental procedure and characterisation

Si, Ti and C elemental compositions were determined by electron probe microanalysis-wavelength dispersive spectrometry (EPMA-WDS on a Camebax equipped with ODPb wavelength dispersive spectrometer, $I = 70$ to 100 nA, $V = 10$ kV, standards = SiC , TiC). Phase identifications were performed by X-ray diffraction (XRD Philips PW 1710, $\text{Co K}\alpha = 1.7902$ Å, 40 kV). XRD was also used to estimate the size of the crystallites. The thickness of the coatings was measured on metallographic cross-sections. Vickers indentations were performed on a Schimadzu apparatus (load range 25-1000 g; five indentations for each load, dwell time = 15 s). Microhardness measurements were performed up to the maximum load available without occurrence of cracks around the Vickers print. Using the empirical relationship [14]: $H_v = H_\infty + \beta d^{-1}$ (d is the diagonal of the indentation print), an "intrinsic" hardness (H_∞) was deduced from the extrapolation at infinite load of the linear regression applied to the data when plotting H_v against $1/d$.

4.- Results

SiC and TiSi₂ were unambiguously identified by XRD. X-ray reflections fitted well in position as well as in intensity with those given in the JCPDS files (TiSi₂, file no.35 - 785 : C54, Orthorhombic and β -SiC, file no. 1-1119). The codeposits were texture-free. The apparent crystallite sizes were estimated from the width at half maximum of the four more intense TiSi₂ diffraction peaks ($d_{311} = 0.230$, $d_{040} = 0.214$, $d_{022} = 0.209$ and $d_{331} = 0.183$ nm.) using the Scherrer's equation [15]. The values deduced ranged between 20 to 50 nm.

Intrinsic hardness monotonically decreased with increasing the volume fraction of TiSi₂ (figure 2), according to the following relation : $H = -15.37 V_{\text{TiSi}_2} + 23.64$. This result is in agreement with a rule of mixture corresponding to the expression:

$$H = V_{\text{TiSi}_2} \cdot H_{\text{TiSi}_2} + (1 - V_{\text{TiSi}_2}) H_{\text{SiC}}$$

where H_{TiSi_2} and H_{SiC} are respectively equal to 7.1 and 24.4 GPa. These values correspond to the intrinsic hardnesses of SiC and TiSi₂ CVD coatings elaborated in the same conditions than the codeposits.

Figure 2 : Variation of the intrinsic hardness as a function of the TiSi₂ volume fraction.

Figure 3: Ln P versus ln c

Sample no 12: 33SiC-67TiSi₂ +
Sample no 3 : 84 SiC-16 TiSi₂ x

Figure 4: l versus load P

Sample no 3

The crack system developed beneath the hardness indentation for this type of materials was typically median-radial [16-18]. As a matter of fact: i) the c/a ratio ($2a$ = the diagonal size of the indentation print and $2c$ = the total length of the median-radial crack) is always close or greater than 2, ii) when plotting $\ln P$ versus $\ln c$ (figure 3), the slopes lie between 1.4 and 1.8, iii) when plotting l ($l = c - a$, the length of the Palmqvist crack) as a function of P , and according to the simple linear relationship: $l = (P - P_0)/4W$, negative values for the load P_0 , corresponding to the microcrack threshold are also obtained (figure 4).

In order to provide an estimate of the toughness (table 1), the formalism of A. Evans and E. Charles [19] was chosen: $K_C = 0,0742 P c^{-3/2}$. The choice of this relation is justified by the fact that we do not have any reliable value of either the elastic modulus (E) or the yield stress (σ_y).

When comparing the values measured on the codeposits with pure SiC- CVD, the toughness is clearly enhanced. An enhancement of 35 % is observed when SiC is the main component, though 50 % is reached when $TiSi_2$ is preponderant.

Table 1 :Toughness values deduced from Evans-Charles formalism.

Codeposit	SiC mol. %	TiSi ₂ mol. %	K _C MPa $\sqrt{m}$
SiC-CVD	100		3.4
n°3	84.5	15.5	4.9
n°4	77	23	4.8
n°12	33	67	5.8

5.- Comparison between experimental results and compositions calculated at thermodynamic equilibrium.

The near-equilibrium conditions that prevail in the gas phase for long residence times and/or high temperatures allow the use of the thermodynamic calculation to determine the nature of the different phases that are formed and look at the influence of various parameters. Though transport phenomena (i.e. motion, energy and mass) and kinetic aspects are neglected, valuable qualitative information is generally obtained.

In order to perform those thermodynamic calculations, the SOLGASMIX program [20] which minimises the Gibbs free energy of the whole chemical system was used. Such a calculation requires the thermodynamic data corresponding to all the species that may form at equilibrium. The thermodynamic data of the 22 gaseous species considered ($SiHCl_3$, $Si(CH_3)_4$, SiH_3Cl , C_4H_{10} , Cl , Cl_2 , $SiCl$, $SiCl_2$, $SiCl_3$, $SiCl_4$, SiH_2Cl_2 , H_2 , SiH , SiH_4 , $TiCl$, $TiCl_2$, $TiCl_3$, $TiCl_4$, CH_4 , C_2H_2 , C_2H_4 , HCl), came from SGTE data bank [21]. In order to estimate the data of the condensed phases, we have assumed that the equilibria in the isothermal section of the Ti-Si-C phase diagram were identical at 850°C to those experimentally established at 1200°C [22] and at 1100°C [23]. Those diagrams, in agreement with our previously calculated section at 1500K [24] (figure 5), show two ternary phases: T_1 which corresponds to the compound Ti_3SiC_2 and T_2 which corresponds to the solubility of carbon in Ti_5Si_3 (maximum solubility at 1100°C, 11 at% [23] or 4 to 6 at% [25]). The solubility of carbon in Ti_5Si_3 at 850°C is not known but it generally decreases with temperature. For our calculation we assumed a maximum solubility of

3at% at 850°C. The solid solution $\text{Ti}_5\text{Si}_3\text{C}_x$ is described, like in our precedent calculation [24], by a quasi-binary approximation between Ti_5Si_3 and C, according to the formalism proposed by Kaufman and Nesor [26].

$$G^{\text{hcp}} = (1 - \alpha) G^{\text{hcp}}_{\text{Ti}_{0.625}\text{Si}_{0.375}} + \alpha G^{\text{hcp}}_{\text{C}} + RT [\alpha \ln(\alpha) + (1 - \alpha) \ln(1 - \alpha)] + X S G^{\text{hcp}}$$

$$\text{where } X S G^{\text{hcp}} = \alpha (1 - \alpha) (A \alpha + B)$$

The coefficients A and B as well as the Gibbs free energy of formation of T_1 (Ti_3SiC_2) were adjusted to represent satisfactorily the equilibria in the isothermal section of the Ti-Si-C phase diagram (which were assumed to be identical to those encountered at 1100 °C) and to respect the 3 at% carbon solubility in Ti_5Si_3 :

$$A = 14357156, B = -986935 \text{ J/g.at}$$

$$\Delta G = -83333 \text{ J/g.at}$$

Lattice stability:

$$^\circ G^{\text{hcp}}_{\text{C}} - ^\circ G^{\text{Graphite}}_{\text{C}} = 114264 - 14.64 T \text{ [27]}$$

Free energy of formation:

$$\Delta G = -72409.5 - 0.31694 T \text{ J/g.at [28]}$$

$$\text{Ti}_{0.625}\text{Si}_{0.375}: \Delta G = -72765 \text{ J/g.at}$$

$$\text{Ti}_{0.606}\text{Si}_{0.364}\text{C}_{0.03}: \Delta G = -85000 \text{ J/g.at}$$

The ΔG variation from Ti_5Si_3 to the maximum solubility of 3% carbon represents an increase of almost 17%.

The Gibbs free energy of formation of the other condensed species came from ref. [28] for the silicon-titanium system (TiSi_2 , TiSi , Ti_5Si_4) and from SGTE data bank [21] for β -SiC and TiC which was considered as a stoichiometric compound. The isothermal section of the Ti-Si-C phase diagram calculated with these data at 1123K is presented in figure 6.

Figure 5: Calculated isothermal section of the Ti-Si-C phase diagram previously calculated at 1200°C [24]

Figure 6: Calculated isothermal section of the Ti-Si-C phase diagram at 850°C

From this set of 30 data, the composition of the solid phases were first calculated at: $P=1$ atm and $T=1123$ K, starting from the compositions of the initial experimental gas phase (table 2).

Table 2: Composition of the condensed phases calculated for nine compositions of the initial experimental gas phase.

Experiment	XH ₂	XTiCl ₄	XSiH ₂ Cl ₂	XC ₄ H ₁₀	% TiSi ₂ Exp.	First calc.	% TiSi ₂ second calc.
6	0.932	0.00565	0.03728	0.02519	0.410	SiC	0.518
7	0.954	0.00434	0.02207	0.01935	0.440	TiSi ₂ +SiC	0.453
8	0.940	0.00570	0.02898	0.02541	0.500	SiC	0.418
9	0.942	0.00395	0.02903	0.02545	0.530	SiC	0.408
10	0.955	0.00301	0.02209	0.01937	0.560	SiC	0.439
11	0.954	0.00434	0.02863	0.01283	0.600	TiSi ₂ +SiC	0.687
12	0.954	0.00434	0.02207	0.01935	0.670	TiC+SiC+C	0.453
13	0.950	0.00575	0.02923	0.01698	0.730	TiSi ₂ +SiC	0.610

In comparison with the experimental codeposited phases, these results (first calculation) indicate a large shift of the compositions towards β -SiC. This divergence, which has already been observed at higher temperature for the TiC-SiC codeposits [29] can be explained by the low pyrolysis kinetics of the hydrocarbon precursor.

In order to cope with that difficulty, the initial gas phase used for the thermodynamic calculation was modified. The kinetic limitation of the pyrolysis of the hydrocarbon precursor was simulated by lowering ten times the amount of C₄H₁₀ in the initial gas phase. A second set of calculations was undertaken using the following compositions i.e. XSiH₂Cl₂, XTiCl₄, XH₂ and 0.1 XC₄H₁₀ normalized by the factor: $1/(XSiH_2Cl_2 + XTiCl_4 + XH_2 + 0.1XC_4H_{10})$. The correspondence between experimental and theoretical compositions is in that case far better. The $\pm 20\%$ dispersion which is observed in figure 7 may account for the experimental reproducibility. Nevertheless, owing to other sources of discrepancy such as the physical phenomena occurring into the reactor which are neglected in the calculation, we can conclude that there is a relatively good correspondence between the predicted and experimental compositions.

Figure 7: Comparison between the calculated and experimental compositions of the deposits.

6.- Conclusion

SiC-TiSi₂ materials of different compositions were codeposited by CVD at atmospheric pressure by varying at 850°C the composition of the input gas mixture: TiCl₄ - SiH₂Cl₂ - C₄H₁₀ - H₂. These composites were texture-free, with apparent crystallite size ranged between 20 to 50 nm. Intrinsic hardness linearly decreased from 24 to 7 GPa with increasing the volume fraction of TiSi₂ from 0 to 100%. In comparison with pure SiC-CVD, an enhancement of at least 35% of the toughness was observed. The influence of the initial gas phase composition was evaluated by comparing the codeposit experimental compositions with those calculated at thermodynamic equilibrium. Despite a lack of experimental reproducibility, enough coherency was reached, by taking into account the kinetic limitation of the hydrocarbon precursor pyrolysis.

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